Increasing Polybrominated Diphenyl Ether (PBDEs) Contamination in Sediment Cores from the Inner Clyde Estuary, U.K.

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Keywords-River Clyde, sediment, flame retardant, estuarine contamination, persistent organic pollutant (POPs)

Abstract The concentrations of 16 polybrominated diphenyl ether (PBDE) congeners in six short sediment cores from the Clyde Estuary were determined by gas –chromatography mass-spectrometry. Total PBDE concentrations ranged from 1 to 2645 μg/kg and the average concentration was 287 μg/kg. BDE-209 was the main congener and varied from 1 to 2337 μg/kg. Elevated total PBDE concentrations were observed close to the sediment surface in the uppermost 10 cm of four of the six sediment cores. Comparison of the down core PBDE profiles revealed that the increase was driven by the accumulation of deca-BDE. Although the deca-BDE mix was dominant, the presence of lower molecular weight congeners BDE-47, BDE-99, BDE-183 and BDE-153 at most sediment intervals suggested additional sources of penta-BDE and octa-BDE pollution. Changing PBDE source input was the major factor in influencing the proportion of nona-brominated congeners, although other explanations such as post burial photo-debromination of BDE-209 cannot be entirely discounted. A clear cascading to lower hepta-, hexa-, and penta- homologues was not found. The increase in total PBDE concentrations and particularly the deca-BDE may possibly be ascribed to the use and subsequent disposal of electrical appliances such as televisions and computers.

In the Clyde sediments the proportion of nona-brominated congeners was higher than that reported for commercial mixtures. This might be due to changing sources of PBDEs or post burial photo-debromination of BDE-209. A clear cascading to lower hepta-, hexa-, and penta- homologues was not found. The increase in total PBDE concentrations and particularly the deca-BDE may possibly be ascribed to the use and subsequent disposal of electrical appliances such as televisions and computers.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), the synthetic compounds used as flame retardants in plastics, polyurethane foams and high impact polystyrene, are found in a multitude of products including televisions, computers, textiles and furniture upholstery (Rahman et al. 2001). PBDEs effectively reduce fire hazards in polymeric materials by releasing bromine atoms which capture OH and H radicals formed during combustion at a temperature approximately 50 °C below ignition temperature of the polymer matrix (Rahman et al. 2001). However, additive flame retardants including PBDEs are not chemically bound to the host polymer and are thus susceptible to leaching into the environment. The presence of PBDEs in sediments is of concern since they can potentially bioaccumulate, transfer up the food web and once ingested by humans may cause thyroid hormone disruption, alter neurodevelopment and interfere with reproductive systems (Talsness 2008).

The three commercial formulations are penta-BDE (DE-71, Bromokal 70-50E), octa-BDE (DE-79 and Bromokal 79) and deca-BDE (Saytex 102E, Bromokal 82-E) (Talsness 2008). The penta- technical formulation is most commonly used in polyurethane foams for furniture and is comprised of 24-38 % tetra- and 40-60 % penta-congeners (BDE-47 and 99) and 4-8% hexa-. The octa-mixture is mainly used in polyamide and polystyrene and is composed of 10-12% hexa-, 44 % hepta-, 31-35 % octa-, 10-11 % nona- and 1 % deca-BDEs with the main congeners BDE-153 and BDE-183 (Alaee et al. 2003). In contrast the deca-mixture (Bromokal 82-E, Great Lakes Chemical Corp. DE-83) is used in commercial textiles and plastics including computer housings and is comprised of ~97% BDE-209 with 3% nona- and octa-BDEs. Severe restrictions on the use (<0.1% of mass for all goods) and marketing of octa-BDE and penta-BDE mixtures in Europe became effective under European law in 2004 and 2006 due to the high bioaccumulation potential (Law et al. 2006). Furthermore the European court of Justice annulled the exemption of deca-BDE in electrical and electronic goods placed on the European union market after June 30th 2008.

Brominated compounds can enter the coastal environment directly from polymer production, through leaching during usage, from waste streams such as incinerators, landfill sites and / or automotive scrap yards as well as from sewage sludge dumping. The accumulation of PBDEs in sediments is not entirely unexpected given their range of physiochemical properties such as low water solubility, low vapour pressures and elevated log K_{OW} values of 5-10 as well as relatively high resistance to biodegradation (Alcock et al. 1993). From a bioacumulative and toxicological standpoint the lower molecular tetra-, penta- and hexa-homologues are more important than the octa- nona-and deca-brominated counterparts (Hale et al. 2001).

The aim of this study was to determine the individual concentration of 16 PBDEs and identify changing congener and homologue group distributions in six short sediment cores from the Clyde Estuary, UK. The focus being to ascertain whether sedimentary hosted PBDE concentrations are on the decline or are increasing.

Materials and Methods

Sample collection

Sediment gravity cores were collected between November 2002 and February 2003 (Fig. 1). Sampling sites in the estuary were accessed using the SEPA vessel 'Endrick II', using pre-determined GPS co-ordinates to locate accurately each position. (Table 1). Each sediment core was refrigerated on the day of collection in order to minimise microbial decay (Rost et al. 2002). Upon return to the laboratory each core was cut in half and sampled at ~10 cm intervals using a stainless steel spatula.

Sample preparation

Sediments were freeze-dried, sieved to pass a brass mesh of aperture 2 mm, the <2 mm ground in an agate Tema mill to <200 μm then ground further in an agate ball mill to <40 μm. Sediments (5-15 g) were spiked with CDE-99, PCB209 and ^{13}C-PCB 141 and extracted with a mixture of acetone and hexane (1:1) for 48 h with a Soxhlet extractor. Activated copper granules were added to the soxhlet flasks during extraction to remove elemental sulfur. Concentrated extracts were cleaned and fractionated on a 10-mm i.d. silica/alumina column packed, from the bottom to top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (2 cm, 3% deactivated), 25% sodium hydroxide silica (5 cm), neutral silica gel (2 cm, 3% deactivated), 50% sulfuric acid silica (8 cm), and anhydrous sodium sulfate (1 cm). The PBDE mixture was eluted with 30 mL of hexane and 60 mL of hexane:methylene chloride (1:1), and the final extract volume was reduced to 500 μL under a gentle N_2 stream. A known amount of internal standard (^{13}C-PCB 208, BDE-118 and BDE128) was added to all extracts prior to instrumental analysis.

Gas Chromatography-Mass Spectrometry

Sample analysis was performed with a Shimadzu Model 2010 gas chromatograph (GC) coupled with a Model QP2010 mass spectrometer (MS) (Shimadzu, Japan) using negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. A DB-XLB (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column (J&W) was used for the determination of PBDE congeners except for BDE-209. The column temperature was initiated at 110 °C (held for 1 min) and increased to 180 °C at 8 °C/min (held for 1 min), 240 °C at 2 °C/min (held for 5 min), 280 °C at 2 °C/min (held for 25 min), and 290 °Cat 5 °C/min (held for 13 min). Manual injection of the 1-μL samples was conducted in the splitless mode and the split mode was turned on after 1 min. Methane was used as a chemical ionization moderating gas at an ion source pressure of 2.4×10^{-3} Pa and helium as the carrier gas at a flow rate of 1 mL/min. The ion source and interface temperatures were set to 200 and 280°C, respectively. For BDE-209, a CP-Sil 13 CB (12.5m × 0.25 mm i.d., 0.2 μm film thickness) capillary column (Chrom pack) was used. The oven temperature was programmed from 110 to 300 °C at a rate of 8 °C/min (held for 20 min) and the high-pressure splitless injection mode was used with a split time of 1 min.

Ion fragments m/z 79 and 81 ($[Br]^-$) were monitored for tri- to hepta-BDEs, and m/z 79, 81, 486.7, and 488.7 for BDE-209. For surrogate standards, m/z 342 and 344 were monitored for CDE-99, m/z 372 and 374 for ^{13}C-PCB 141 and m/z 498, and 500 for PCB 209. In addition, m/z 476, and 478 were used for the internal standard (^{13}C-PCB 208) and m/z 79, 81 for BDE-118 and -128. Quantification of tri- to hepta-BDEs was carried out with the internal calibration procedure, whereas BDE-209 was quantified with the external standard method. Peaks were quantified only if the signal/noise > 3 and the ratio between two monitored ions was within 15% of the standard value. BDE-85 was not quantified due to chromatographic interference in some of the samples. The limit of detection (LOD), defined as a signal of 3 times the noise level, ranged from 0.01 to 0.04 ng/g for all congeners except for BDE-209, when 10 g of dry sediment was extracted. The LOD for BDE-209 was 1 ng/g.

For each batch of 20 field samples, a procedural blank (solvent with a filter paper identical to that used to wrap the sediment), a spiked blank (11 PBDE congeners spiked into solvent with the filter paper), and a sample duplicate were processed. Only small concentrations of BDE-47 and -99 were found in procedural blanks, and they were appropriately subtracted from those in the sample extracts. Recoveries of 11 PBDEs congeners (BDE-28, -47, -66, -100, -99, -85, -154, -153, -138, -183, and -209) ranged from 86.4 ±13.2% in five spiked blank samples. Reported concentrations were not surrogate recovery corrected. ΣPBDEs values were determined from the sum of the peak areas of BDE-28, -47, -66, -100, -99, -85, -154, -153, -138, -183, -197,-203,-196,-208, -207 and 209; homologue group concentrations were determined from the appropriate congener(s).

Results and Discussion

Concentrations and distribution

The ΣPBDEs and ΣPBDEs (except BDE-209) from six sediment cores are presented in Fig. 2 and the concentration of nona- to penta-BDE shown in Fig. 3. Total PBDE concentrations ranged from 1 to 2645 µg/kg dry weight and the ΣPBDEs except BDE-209 ranged from 1 to 307 µg/kg (Fig. 2). The concentration of BDE-209 varied from 1 to 2337 µg/kg and comprised on average 80 % of all BDEs measured. The concentration of BDE-209 was higher than that of the summed concentrations of tri-, tetra-, penta-, hexa- and hepta-homologue groups in all the sediments as exemplified by the typical PBDE homologue group concentrations presented in Fig. 4. Recent studies of four sediment cores from the Garroch Head sewage disposal site in the Firth of Clyde (located approximately 32 Km downstream of site 6) reported higher values of <LOD to 23.4 µg/kg (Σ17PBDEs except BDE-209) and 2.3 to 98125 µg/kg (BDE-209) (Webster *et al.* 2008). However, substantially lower values of <LOD (Σ17PBDEs except BDE-209) and 3.5 to 5.5 µg/kg (BDE-209) for a sediment grab (Pladda) located on the southern tip of the Isle of Arran were also documented (Webster et al. 2008). Similarly highly polluted river and coastal sites in the UK such as the river Tees <0.3-368 (BDE-47) and <0.6-898 (BDE-99) have higher concentrations of individual PBDE congeners than those observed in this current study of the inner Clyde (Allchin et al. 1999; Law et al. 2006). In this current study the ΣPBDEs (except BDE-209) concentrations 1 to 307 µg/kg from sediment cores are greater than those reported for the Garroch Head sewage dump sites but contain far lower concentrations of BDE-209. One plausible explanation for this difference is that the six sites reported in this work have not been impacted by direct dumping of sewage sludge (Law et al. 2006; Wang et al. 2007). Also, it is probable that PBDE concentrations encountered in these inner estuarine sediment cores are derived in the main from landfill sites, heavy and light industry and discharge from municipal sewage works with a minor aeolian sourced background.

On a world wide basis the PBDE concentrations reported in this study are broadly comparable to those of surface sediments of the Pearl River Delta (Σ17PBDEs except BDE-209) 0.04 to 94.7 µg/kg and BDE-209 of 0.4 to 7340 µg/kg but are considerably higher than the Scheldt estuary and North Sea coastal sediments (ΣPBDEs except BDE-209) 0.4-0.6 and BDE-209 1-32 µg/kg (Klamer et al. 2005; Mai et al. 2005). No systematic change in PBDE concentrations were observed from Princes Dock (1) to Greenock (6) suggesting that the PBDE pollution was derived from multiple sources as compared to a single point source (Fig. 2).

Down profile variation in PBDE concentrations

The highest concentration of ΣPBDE 307 µg/kg and BDE-209 2337 µg/kg was observed at the confluence of the river Cart and the Clyde, opposite Clydebank shipyard at Station 4 at a depth 5-10 cm and the lowest PBDE concentrations were observed at station 2 near Partick. A recent study of polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCBs) in surface sediments from the Clyde estuary also showed higher levels of contamination associated with sediments close to dockyards as compared to the main channel (Vane et al. 2007a). Inspection of the down core BDE-209 profiles revealed low concentrations at the base of all six sediment cores, however for stations 1, 3, 4 and 6 these concentrations gradually increased to a maximum of 726, 419, 2337 and 795 µg/kg at or close to the surface (0-10cm) (Fig. 2). For example, BDE-209 values at Station 1 ranged from 5 µg/kg at 67 cm to 59 µg/kg at 28 cm then increased fairly smoothly to 137 µg/kg at 18 cm after which a rapid rise to 718 µg/kg at 8 cm was observed before reaching maximum values 727 µg/kg and levelling off at the surface (Fig. 2). In general, stations 3, 4 and 6 showed similar changes in BDE-209 concentrations whereas the BDE-209 concentrations at station 2 varied in a non-systematic manner yielding a narrow range of lower values from 2 µg/kg at 22 cm to 116 µg/kg at 32 cm (Fig. 2). In contrast, a third type of BDE-209 profile at station 5 showed maximal BDE-209 values of 998 µg/kg as well as slightly elevated ΣPBDE concentrations at ~35 cm (Fig. 2).

No uniform change of PBDE concentrations with depth was observed at station 2. This could be due to vertical sedimentary mixing such as that reported in short sediment cores from North of Ellesmere port on the Mersey estuary, UK, (Vane et al. 2007b). Although other processes such as diffusion cannot be entirely discounted they are unlikely given the low aqueous solubility and hydrophobic nature of PBDEs as defined by their log K_{ow} values. Similarly, for Station 5 the subsurface BDE-209 maximum centred at 35 cm could be attributable to overturn of sediments during dredging of the main channel, sediment movement during storm events and / or possibly by a single discharge event (Figs. 2 and 3). With the exception of station 5 comparison of the ΣPBDE (excluding BDE-209) to BDE-209 profiles revealed a subtle mirroring of the concentration patterns up core confirming the notion that PBDE concentrations were highest at or just below the sediment surface and indicating that the PBDEs were derived from similar sources (Fig. 2 & Fig 3).

PBDE congener and homologue group patterns

Overall, four of the six BDE-209 concentration depth profiles suggested that PBDEs and particularly the deca-BDE mixture which is mainly comprised of ~97% BDE-209 are accumulating in the uppermost 0-10 cm of the inner Clyde estuary. An increasing trend in environmental concentrations of PBDE and BDE-209 from 1970 to the mid-1990s has been reported in sediment cores from the Wadden Sea (Netherlands), Drammenfjord (Norway), Lake Woserin (Germany) and Pearl River Delta (China) and was attributed to increasing PBDE production and in the latter case, the recent growth of the electronics industry in Southern China (Mai et al. 2005; Zegers et al. 2003). In the present study the predominance and accumulation of BDE-209 close to the surface in Clyde sediments are commensurate with the greater historical production of Deca-mix PBDE formulation and the European ban of Octa- and Penta-mix formulations in 2004 (Law et al. 2006). Although the deca-BDE are now banned in electrical goods sold in Europe it is unlikely that sedimentary concentrations will rapidly decline given the environmental persistence of PBDEs and widespread usage in industrial and consumer products. This idea is supported in part by the fact that structurally similar PCB compounds are still found in estuarine sediments despite manufacture being prohibited in UK 1977 and total cessation of usage in closed low volume equipment in 2000.

The predominance of BDE-209 over other congeners in Clyde sediments is entirely consistent with recent environmental health studies of UK domestic indoor dusts which contained BDE-209 at concentrations as high as 45,000 µg/kg (Harrad et al. 2008). Although the deca-BDE was clearly dominant, the presence of BDE-47 and BDE-99 at all depths also suggested input from sources containing the commercial penta-product and similarly the presence of BDE-183 and BDE-153 in the majority of the sediments confirmed a contribution from the commercial octa-BDE product.

Nona-brominated congeners (BDE-206,-207,-208) were the second most abundant homologue group after deca-BDE and comprised on average 11% by weight of the total BDE inventory (Fig. 5). Previous characterisation by GC/MS of technical deca mixtures have shown that these are comprised of 0.3 to 8 % by weight depending on the specific formulation, therefore the relative amount of nona-BDE observed here was greater than would be expected from the original technical formulations (Alaee et al. 2003; Hoh & Hites 2005). One explanation could be that BDE-209 had undergone debromination to yield a relative increase in nona-BDE. Laboratory photodegradation studies have demonstrated stepwise debromination of deca-BDE to nona-, octa-, hepta- and hexa- homologues (Soderstrom et al. 2004). Alternatively, the higher proportion of nona-BDE than expected from deca formulations alone could be due to an octa-BDE source such as DE-79 (Great Lakes Chemical Corp.) which was comprised of 25 % by weight nona-BDE, however other octa-BDE formulations have much lower proportions of nona-BDE (Alaee et al. 2003).

Comparison of the downcore BDE-99 and BDE-47 concentration revealed that the proportion of BDE-99 to BDE-47 was greater than or equal to unity for 49 of the 71 sediment intervals (Fig. 5). The majority of the 22 sediments with higher concentrations of BDE-47 as compared to BDE-99 were observed toward the base of the sediment cores at stations 1, 2, and 6. In contrast cores at stations 3, 4 and 5 contained more BDE-99 to BDE-49 at most depths. Commercial penta-BDE mixtures such as BromoKal 70-5DE and Great Lakes Chemicals DE-71 are comprised of approximately equal amounts of BDE-99 and BDE-47 to give a BDE-99:BDE-47 ratios of ~1 and 0.7 respectively (Hale et al. 2001; Hassanin et al. 2004; Hoh & Hites 2005; Mai et al. 2005). However, a number of PBDE studies have reported the preferential decrease in BDE-47 compared to that of other congeners in soils and sediments which have received the penta-BDE mix including BDE-99 (Allchin et al. 1999; Hassanin et al. 2004; Mai et al. 2005). This change was postulated to be due either to the slightly higher octanol/water partition coefficient of BDE-99 as compared to BDE-47 or to greater degradation of BDE-47 and / or aeolian transport effects (Hale et al. 2001; Hassanin et al. 2004). In the current study the higher concentration of BDE-99 to BDE-47 in the upper most 10 cm of all the cores may also be due to the preferential degradation of BDE-47, in contrast the greater proportion of BDE-47 to BDE-99 observed at stations 1, 2, and 6 may be due to changes in local source input.

Acknowledgements

Sincere appreciation is expressed to Staff at the Scottish Environment Protection Agency (SEPA) and particularly captain Hugh Anderson and technicians John Derrick and James Glendinning of the SEPA vessel ‘Endrick II’. We also thank BGS staff J Ridgway, T R Lister and M H Strutt for core collection. Nigel Birch at the

British Consulate-General, Guangzhou provided logistic support to C.H. Vane during two visits to Guangzhou in 2006-7. This paper is published by permission of the Executive Director, British Geological Survey.

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Fig 1. Location of sediment cores sampled within the inner Clyde Estuary UK.

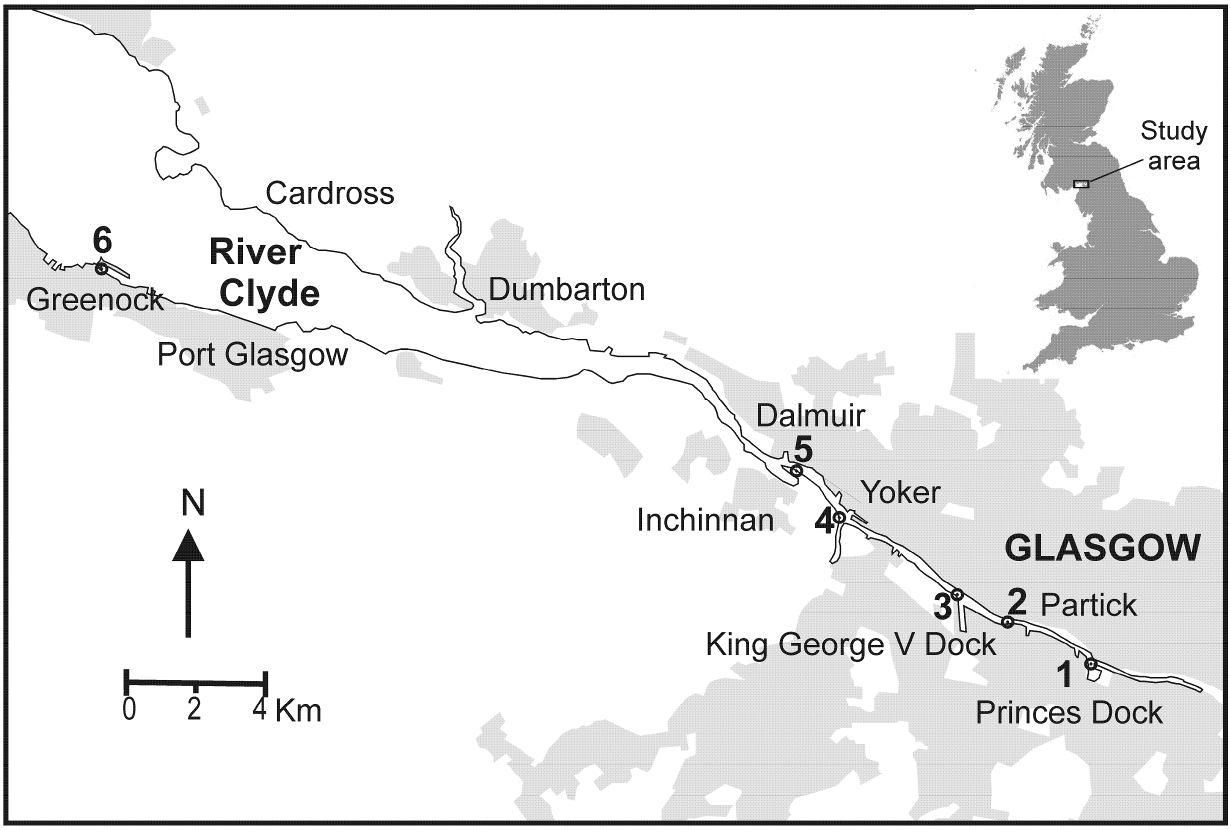
Fig 2. Variation of ΣPBDE, ΣPBDE (except BDE-209) and BDE-209 concentrations with depth for sediment cores from the inner Clyde Estuary.

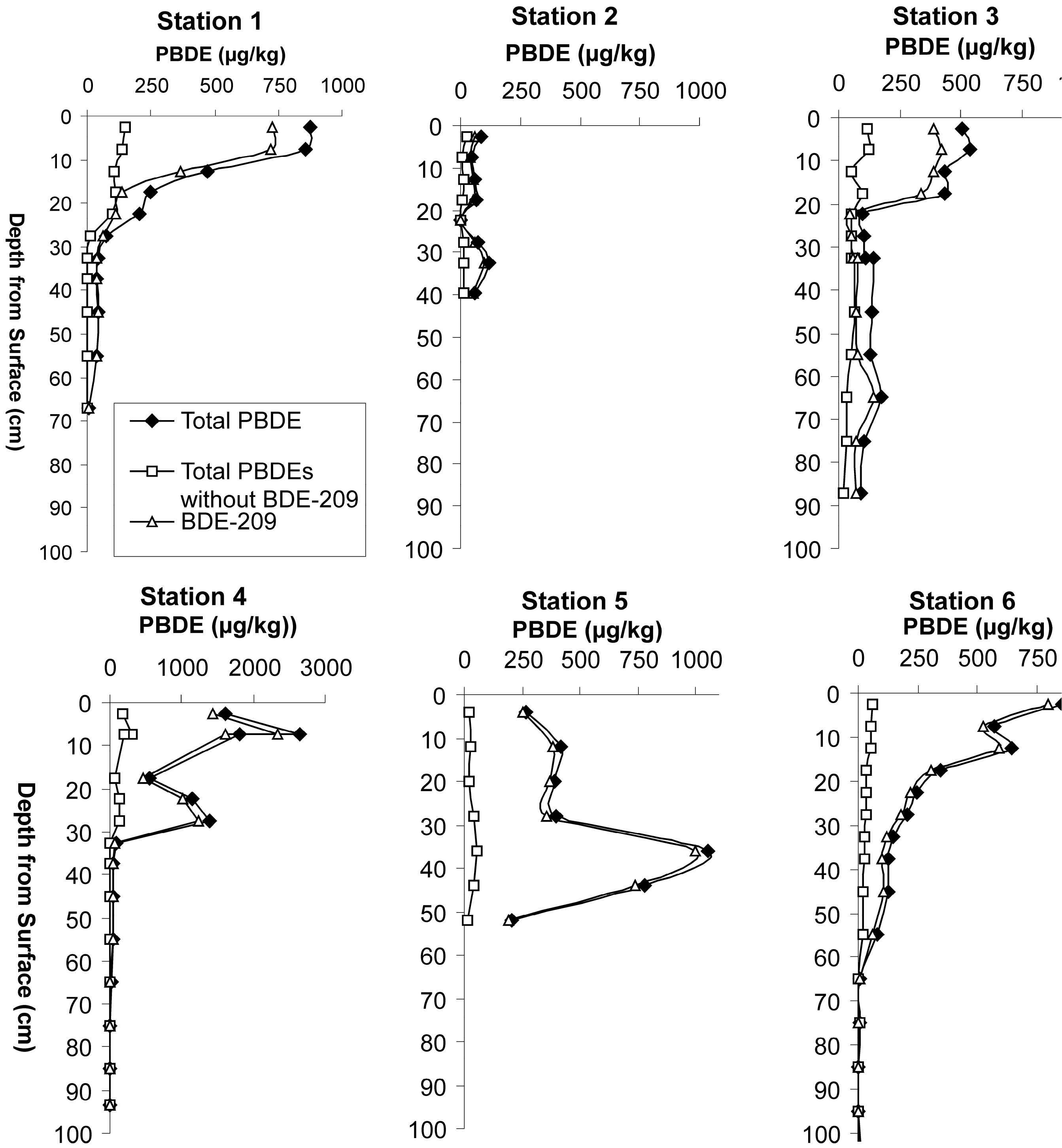
Fig 3. Variation of different PBDE homologue groups down core.

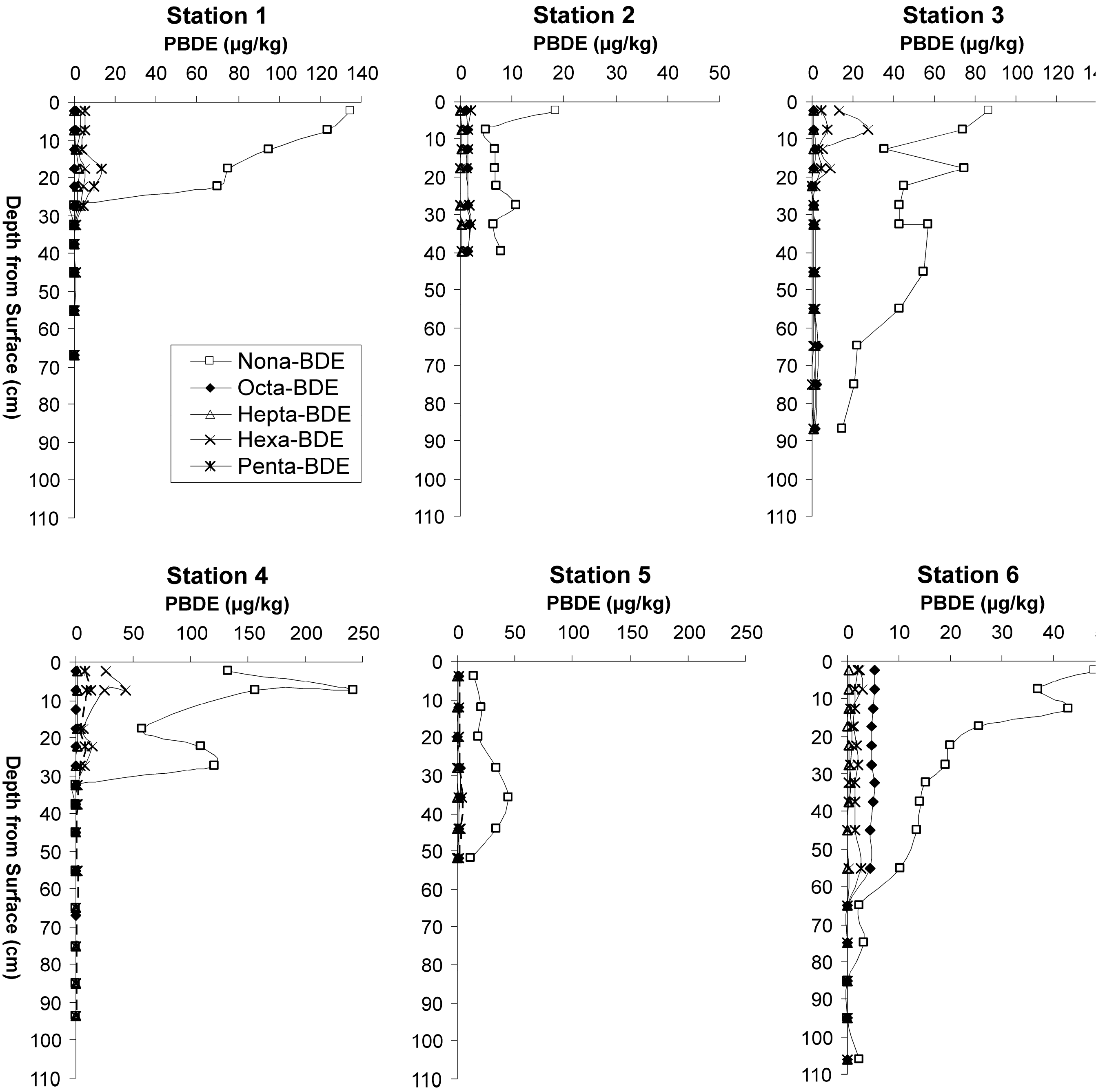
Fig 4. Typical PBDE profile of sediment from the Clyde Estuary.

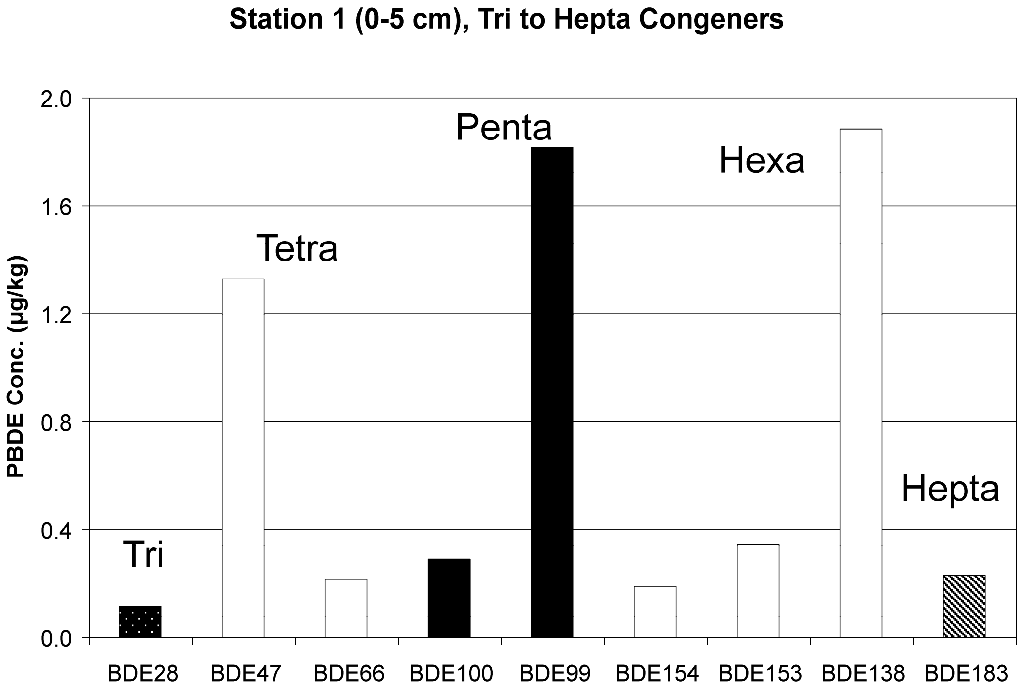
Fig 5. Comparison of BDE-47 and BDE-99 concentrations in sediment cores from the Clyde Estuary.

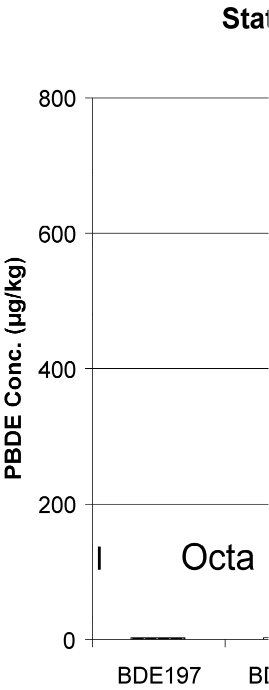
Table 1. Location of sample sites from the Clyde Estuary.

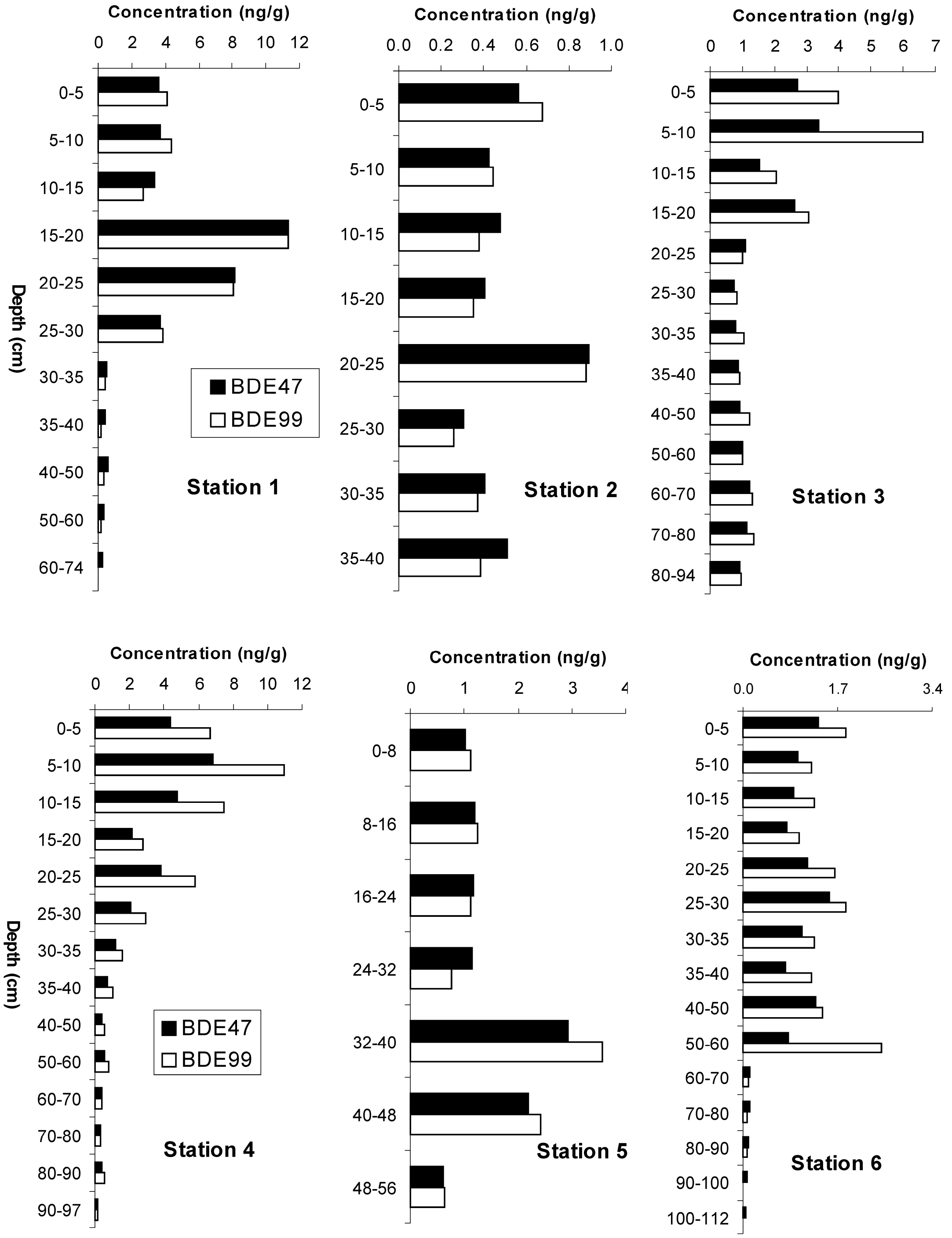

Study area
Cardross
River Clyde
6
Greenock
Dumbarton
Port Glasgow
Dalmuir
5
Yoker
Inchinnan
4
N
GLASGOW
3
2
Partick
King George V Dock
1
Princes Dock
0
2
4
Km


Station 1
PBDE (µg/kg)
0
250
500
750
1000
Depth from Surface (cm)
0
10
20
30
40
50
60
70
80
90
100
Total PBDE
Total PBDEs without BDE-209
BDE-209
Station 2
PBDE (µg/kg)
0
250
500
750
1000
Station 3
PBDE (µg/kg)
0
250
500
750
Station 4
PBDE (µg/kg))
0
1000
2000
3000
Depth from Surface (cm)
Station 5
PBDE (µg/kg)
0
250
500
750
1000
Station 6
PBDE (µg/kg)
0
250
500
750


Station 1
PBDE (µg/kg)
0 20 40 60 80 100 120 140
Depth from Surface (cm)
0 10 20 30 40 50 60 70 80 90 100 110
Nona-BDE
Octa-BDE
Hepta-BDE
Hexa-BDE
Penta-BDE
Station 2
PBDE (µg/kg)
0 10 20 30 40 50
Station 3
PBDE (µg/kg)
0 20 40 60 80 100 120
Station 4
PBDE (µg/kg)
0 50 100 150 200 250
Depth from Surface (cm)
Station 5
PBDE (µg/kg)
0 50 100 150 200 250
Station 6
PBDE (µg/kg)
0 10 20 30 40


Station 1 (0-5 cm), Tri to Hepta Congeners
PBDE Conc. (µg/kg)
2.0
1.6
1.2
0.8
0.4
0.0
Tri
Tetra
Penta
Hexa
Hepta
BDE28
BDE47
BDE66
BDE100
BDE99
BDE154
BDE153
BDE138
BDE183


PBDE Conc. (µg/kg)
800
600
400
200
0
Octa
BDE197


Concentration (ng/g)
0 2 4 6 8 10 12
Depth (cm)
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-50
50-60
60-74
■ BDE47
□ BDE99
Station 1
Concentration (ng/g)
0.0 0.2 0.4 0.6 0.8 1.0
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
Station 2
Concentration (ng/g)
0 1 2 3 4 5 6 7
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-50
50-60
60-70
70-80
80-94
Station 3
Concentration (ng/g)
0 2 4 6 8 10 12
Depth (cm)
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-50
50-60
60-70
70-80
80-90
90-97
■ BDE47
□ BDE99
Station 4
Concentration (ng/g)
0 1 2 3 4
0-8
8-16
16-24
24-32
32-40
40-48
48-56
Station 5
Concentration (ng/g)
0.0 1.7 3.4
0-5
5-10
10-15
15-20
20-25
25-30
30-35
35-40
40-50
50-60
60-70
70-80
80-90
90-100
100-112
Station 6

Station Number	BGS core code	Latitude (decimal degrees)	Longitude (decimal degrees)
1	610	55.858	-4.726
2	573	55.869	-4.331
3	615	55.874	-4.353
4	616	55.892	-4.405
5	562	55.901	-4.418
6	608	55.945	-4.726